Pilot Demonstration of Technology for the Production of High Value Materials from the Ultra-Fine ($PM_{2.5}$) Fraction of Coal Combustion Ash

Semi-Annual Status Report

Reporting Period Start Date: January 21, 2006

Reporting Period End Date: July 20, 2006

Principal Authors: R. S. Perrone, J. G. Groppo, T. L. Robl,

Report Issued: August 30, 2006

DOE Contract No. DE-FC26-03NT41726

Center for Applied Energy Research
University of Kentucky
Lexington, KY 40511

Disclaimer

Abstract

Three types of chemically and functionally different thermoplastic polymers have been chosen for evaluation with the fly ash derived filler: high density polyethylene (HDPE), thermoplastic elastomer (TPE) and polyethylene terephthalate (PET). The selections were based on volumes consumed in commercial and recycled products. The reference filler selected for comparison was 3 μm calcium carbonate, a material which is commonly used with all three types of polymers.

A procedure to prepare filled polymers has been developed and the polymer/filler blends have been prepared. Selected samples of filled polymers were subjected to SEM analysis to verify that the fly ash derived filler and the calcium carbonate were well dispersed.

Material taken from a utility ash pond was classified using a novel combination of hydraulic and lamellar classifiers to produce an ultra-fine ash product. This product was dried and used in a series of tests to determine its potential as a filler in plastics. The general properties of the ultra-fine ash from several runs are as follows:

- D_{50}: 3 – 5 μm
- Specific gravity: ~2.41
- Loss on ignition: 2 – 3 %
- Carbon content: 1-2%
- Color: dark grey on content: 1 – 2%
- Morphology: spherical

The addition of fillers increased the modulus of the HDPE composite, but decreased both the offset yield stress and offset yield strain, showing that the fillers essentially made the composite stiffer but the transition to plastic deformation occurred earlier in filled HDPE as stress was applied. Similar results were obtained with TPE, however, the decrease in either stress or strain at offset yield were not as significant. Dynamic mechanical analyses (DMA) were also completed and showed that although there were some alterations in the properties of the HDPE and TPE, with the addition of $CaCO_3$ and fly ash, the alterations are small, and more importantly, transition temperatures are not altered.

A utility patent on the design of the hydraulic classifier, described extensively during our last reporting period, was written and filled with the U. S. Patent and Trademark Office during the period.

Executive Summary

Filler is a solid material used in a plastic at a high volume loading, usually over 5%, in order to produce a composite with improved characteristics over the pure polymer. Improvement may be in performance, weight, cost or ease of manufacture and may come at the cost of a tradeoff in some other characteristic. For example, cost may be reduced at the expense of flexural strength in a part for which flexural strength is not critical. Consequently, the evaluation of the suitability of any filler must be in the context of a particular application. In the absence of such context, a filler can only be evaluated in terms of how various characteristics change by its addition.

Ultra-fine fly ash is readily obtainable from ash ponds as a product of the hydraulic classification scheme developed at CAER. It has a low carbon content, is chemically inert with respect to plastics and has a generally spherical shape. This last characteristic differentiates it from other mineral fillers and may permit the composites to maintain low viscosity which will facilitate processing even at high filler loadings.

The bonding of the filler to the polymer is critical to integrating the filler in the composite. Untreated fly ash has a glassy surface which does not bond well to the polymer; this is also typical of mineral fillers. In practice, the bonding of filler to polymer is enhanced by a coupling agent such as organofunctional silanes or titanates, which bind to the surface of the filler chemically via hydrolysis and extend an organic "tail" out from the surface. This promotes wetting of the filler by the polymer and improves the composite performance.

A procedure was developed to produce plastic composite films and was used to make films comprised of two thermoplastic polymers; high density polyethylene (HDPE) and thermoplastic elastomer (TPE). Filled and un-filled films were prepared using ultra-fine fly ash ($d_{50} \approx 3.5\mu m$) and similarly sized commercial grade calcium carbonate (Omya PW-3) for comparison. Stress/strain curves were generated for the composite films as well as dynamic mechanical analysis (DMA).

Results showed that the addition of fillers increased the modulus of both the HDPE and TPE composites, but decreased both the offset yield stress and offset yield strain, indicating that the fillers made the composites stiffer, but the transition to plastic deformation occurred earlier as stress was applied. DMA results showed that although there were some alterations in the properties of the HDPE and TPE with the addition of $CaCO_3$ and fly ash, the alterations are small, and more importantly, transition temperatures are not altered.

A utility patent titled "Method for Hydraulically Separating Carbon and Classifying Coal Combustion Ash" was written and filled with the USPTO on June 13, 2006. It was assigned the number S.N. 11/451,652 and is now pending.

Contents Page

Results and Discussion

The results and discussion of progress made during this reporting period are summarized in this section, which is organized by Task and Subtask. For clarity, major accomplishments of each Task or Subtask are highlighted with a narrative description of specific activities.

Task 1 – Feedstock Evaluation.

The objectives of this task are to obtain the necessary data to finalize equipment selection for the PDU design and the reagent requirements to produce high quality filler and super pozzolan from both dry ESP ash and pond ash.

Subtask 1.1 Sample Procurement

Status: *Essentially Completed.*

Subtask 1.2 Sample Characterization

Status: Essentially Completed.

Subtask 1.3 Evaluation of Dispersion Parameters

Status: Essentially Completed.

Subtask 1.4 Testing of Processing Parameters

Status: Essentially Completed.

Subtask 1.5 Process Simulation.

A patent application was written and submitted to the U.S. Patent and Trademark Office (USPTO) during the period. The patent application "Method for Hydraulically Separating Carbon and Classifying Coal Combustion Ash" received by the USPTO on June 13 and assigned the number S.N. 11/451,652 and is now pending. In addition an application with the USPTO was filed under the Patent Cooperation Treaty (PCT) and received on June 29, 2006, which will allow foreign patents to be filled for the invention by December 13, 2008. The application covers the design of the hydraulic classifier that was extensively described in our last technical report.

Task 2. Pilot/Demonstration Plant Final Design.

Subtask 2.1 PDU Conceptual Design of PDU Facility.

Status: Essentially Completed

Subtask 2.2 PDU Construction of PDU Facility.

No activity this period.

Task 3. Pilot/Demonstration Plant Operation.

No activity this period.

Task 4. Product Evaluations and Final Economic Evaluation

Subtask 4.1 Commercial Scale Final Design

No Activity this period.

Subtask 4.2 Product Testing.

Subtask 4.2.1 Superpozzolan Testing.

Status: Essentially Completed.

Subtask 4.2.1 Filler Testing.

Preparation of Fly Ash Derived Filler

A very fine filler was prepared by processing ash from a utility fly ash pond with hydraulic classification system employing a novel combination of hydraulic and lamella classifiers. The fly ash was dewatered to 65 – 75% solids and then dried to a powder. The general properties of the filler from several classifier runs are as follows:

- D_{50}: 3 – 5 μm
- Specific gravity: ~2.41
- Loss on ignition: 2 – 3 %
- Carbon content: 1 – 2%
- Morphology: spherical
- Color: dark grey

Preparation of Filled Polymer Systems

Three types of chemically and functionally different thermoplastic polymers have been chosen for evaluation with the fly ash derived filler. These polymers were selected because they are used in large volumes in commercial and recycled products, and therefore offer the greatest opportunity for utilization. The three thermoplastic polymers are:

- Dow HDPE DMDA-8907 NT 7 high density polyethylene (HDPE)

- Santoprene 55 thermoplastic elastomer (TPE), and
- Dupont Crystar 3946 polyethylene terephthalate (PET).

The reference filler selected for comparison was 3 μm calcium carbonate (Omya PW-3), a material which is commonly used with all three types of polymers.

Filled polymer systems were prepared with a Haake PolyLab System (Rheomix 3000p) mixer using R3000 (roller-rotor) mixing blades. The preparation procedure was described in a previous report. To date, HDPE and TPE systems have been prepared and tested.

Test Film Preparation and Analysis

Filled polymer composites were prepared with a Haake PolyLab System (Rheomix 3000p) mixer using R3000 (roller-rotor) mixing blades. For each composite, the mixer was first heated to a temperature of 5°C above the melting or softening point of the polymer, and then the polymer was added with the mixer operating at 20 rpm. After approximately 10 minutes of mixing, the filler was introduced into the melt over a 30 – 60 second period. The total mixing time ranged between 25 and 70 minutes depending on the polymer and filler type. Generally, mixing was terminated 15 to 20 minutes after the torque reading from the mixer stabilized at a minimum after filler addition

After cooling, the melt was ground into particles typically less than 6 mm in size. The ground polymer was used to prepare films for testing. The films were prepared in a Carver Laboratory Press with heated platens. A measured quantity of composite was placed between two sheets of a fiber reinforced Teflon film separated by shims. The sandwich was then placed in a bag made of the same material, sealed and evacuated to 25-27" Hg. The bag was placed between the platens which had been heated above the melting/softening point for 5 minutes, and then pressure applied to spread the composite and form a film with a uniform thickness controlled by the shims. Upon cooling, the films were die cut into "dumbbell" specimens according to ASTM D 638-99 Type V. The specimens were tested in an MTS QTest 10 tensile tester. The average over ten specimens are reported here. Figures 1 thru 3 show the results of the tests done on HDPE. The error bars represent one standard deviation.

Figure 1 shows how the modulus changes with the addition of fillers. The modulus is the slope of the stress/strain curve expressed in MPa defined where the relationship is linear and essentially represents stiffness or resistance to stretching. The stress/strain point at which material behavior changes from elastic to plastic is known as the Yield Point. Because of the practical difficulty of locating this point, the Offset Yield Point is used in tabulations of material properties. At the Offset Yield Point the sample has deformed plastically to an extent that will leave the material with a permanent strain of 0.002 (0.2%) when it is at zero stress. The stress at which this occurs is the 'offset yield stress'; the 'offset yield strain' is similarly derived, as illustrated in Figure 4. The addition of fillers increased the Modulus of the HDPE composite, but decreased the Offset Yield Stress (Figure 2) and Offset Yield Strain (Figure 3). These results show that the fillers essentially make the composite stiffer (i.e. increased

Modulus), but the transition to plastic deformation occurs earlier in filled HDPE as stress is applied.

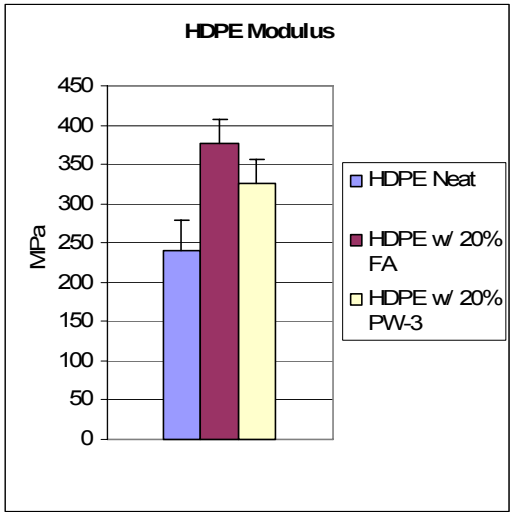


Figure 1. HDPE Modulus.

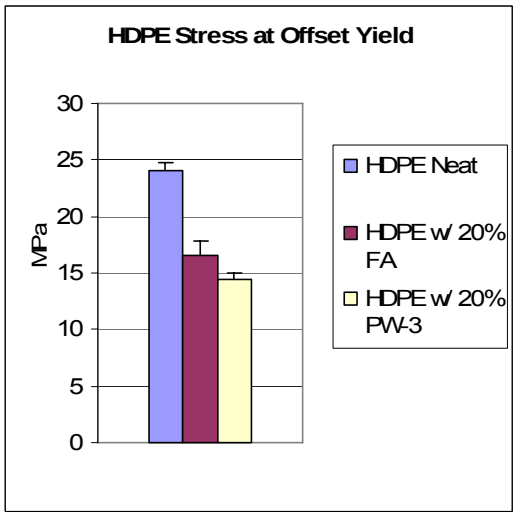


Figure 2. HDPE Stress at Offset Yield.

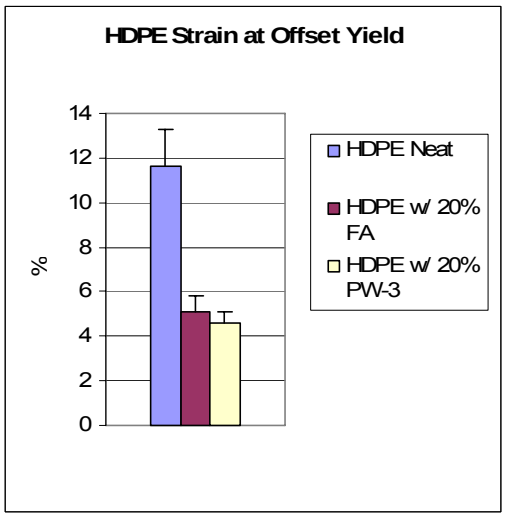


Figure 3. HDPE Strain at Offset Yield.

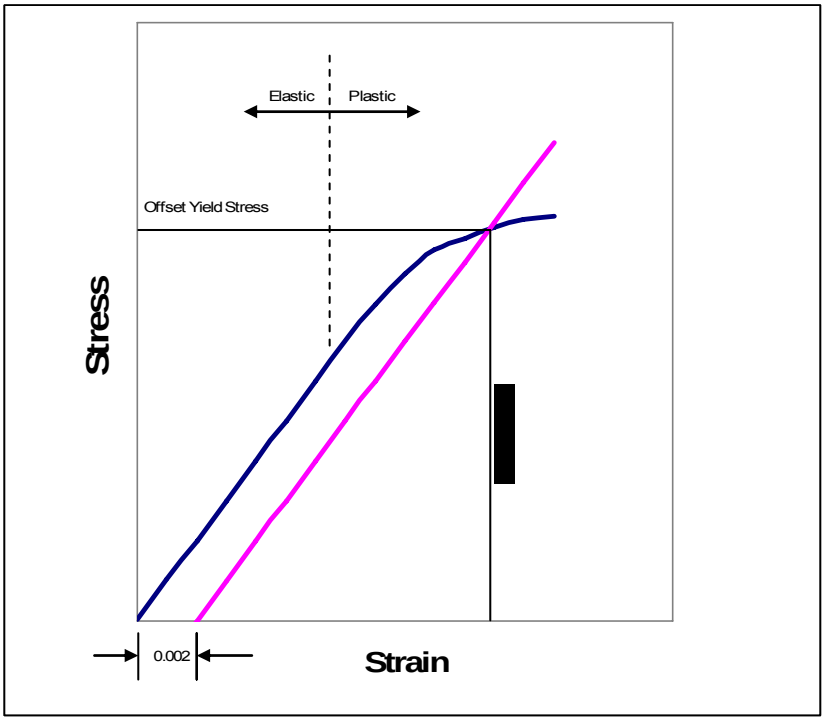


Figure 4. Schematic Illustration of Offset Yield Point.

Similar evaluations were conducted on composites made with Santoprene 55 thermoplastic elastomer (TPE). Elastomers exhibit a very short linear segment and no clearly definable yield point. Consequently, the tensile strength is typically characterized simply by the offset yield stress and strain; results are shown in Figures 5 and 6. As with results obtained for HDPE, the offset yield strain decreased with the addition of increasing amounts of filler, however, the decrease in either stress or strain at offset yield were not as significant for TPE. Also apparent from these results is that while fly ash and calcium carbonate fillers did decrease stress at offset yield for TPE composites, the decrease remained constant at filler loadings up to as high as 50%. However, strain decreased with increased filler loading.

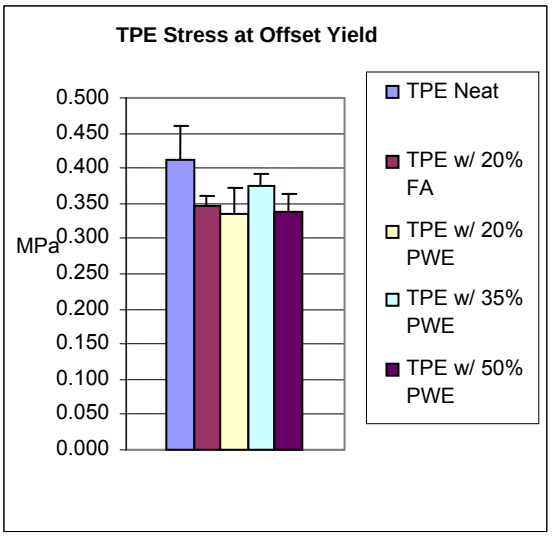


Figure 5. TPE Stress at Offset Yield.

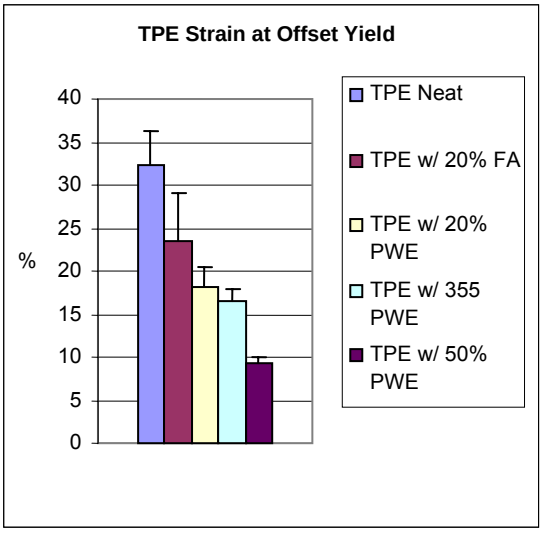
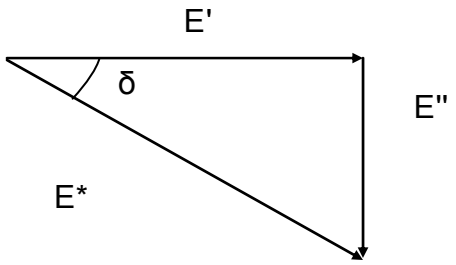


Figure 6. TPE Strain at Offset Yield.

Dynamic mechanical analysis (DMA) refers to a several ways of examining a material's properties. For example, a periodic, sinusoidal stress can be applied to a material and the strain measured or the strain may be controlled and the stress measured. Simultaneously, the frequency of the oscillation or the specimen temperature may be varied. If the material is perfectly elastic, then the stress and strain curves will be exactly in phase, that is, the maximum deformation will occur when the maximum force is applied. For a purely viscous material the two curves will be 90° out of phase, that is, the material will continue to deform as long as a force is present so that it reaches the maximum deformation as the force approaches zero. A viscoelastic material will produce a stress curve that is displaced from the strain curve by some phase angle, δ. The viscous, or loss, modulus E'' is the imaginary component of the complex modulus E* :



If there is no viscous behavior, then E''= 0, δ = 0 and E' = E*. For the analyses done here, the ratio tan delta (= E"/E') is usually plotted against temperature along with both the storage and loss moduli.

E' correlates with the mobility of the polymer molecules within the bulk structure. Molecules with little potential for movement, or 'free volume', present a stiffer structure than if localized bond movements (bending and stretching) are possible. As the temperature increases, energy becomes available to overcome the activation barriers to

various classes of motion. These transition temperatures may be seen on the E' vs. Temp plot as drops in the E' and vary with the polymer/composite being tested.

At the glass transition, T_g, the free volume increases to permit large scale molecular motion. The T_g is a critical feature of the polymer and usually defines a limit of the operating temperature range of the material. If strength and stiffness are required, it is the upper limit; for elastomers it is the lower limit.

In the following procedures, a specimen of each material was subjected to a periodically oscillating tensile strain of 3% at 1 Hz and the stress recorded as the temperature varied at a rate of 3 °C/min from -150 °C to a temperature near the melting point. The specimens were cut from the same films as those used in tensile strength testing and were approximately 15 mm by 5 mm and 0.4 mm thick.

Figures 7, 8 and 9 show the data for HDPE and HDPE composites.

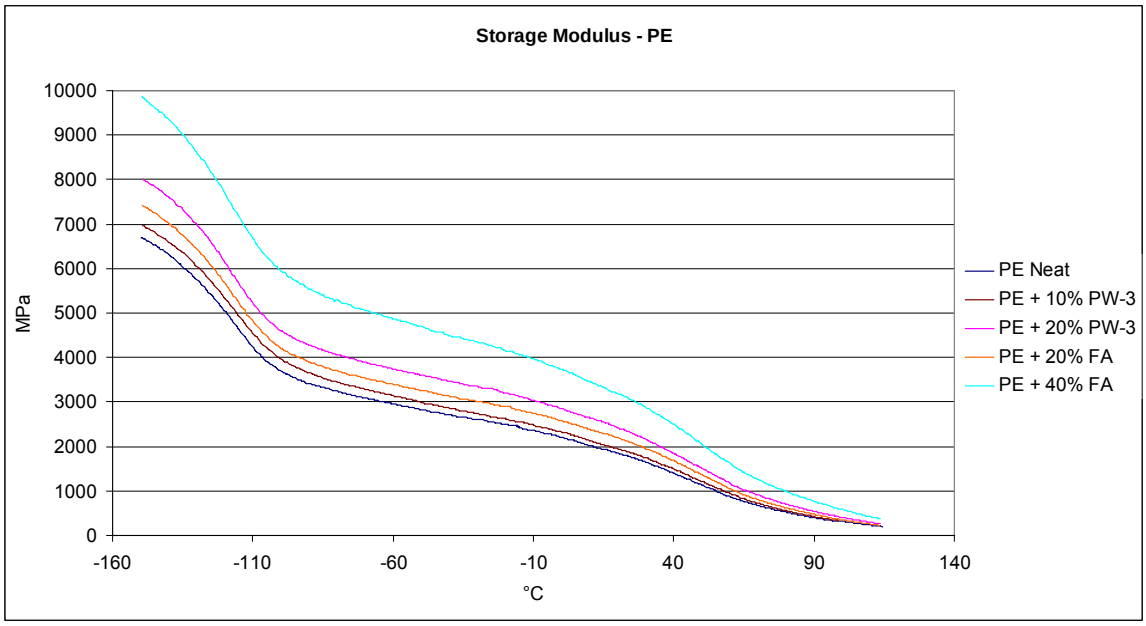


Figure 7. Storage Modulus for HDPE and Filled Composites.

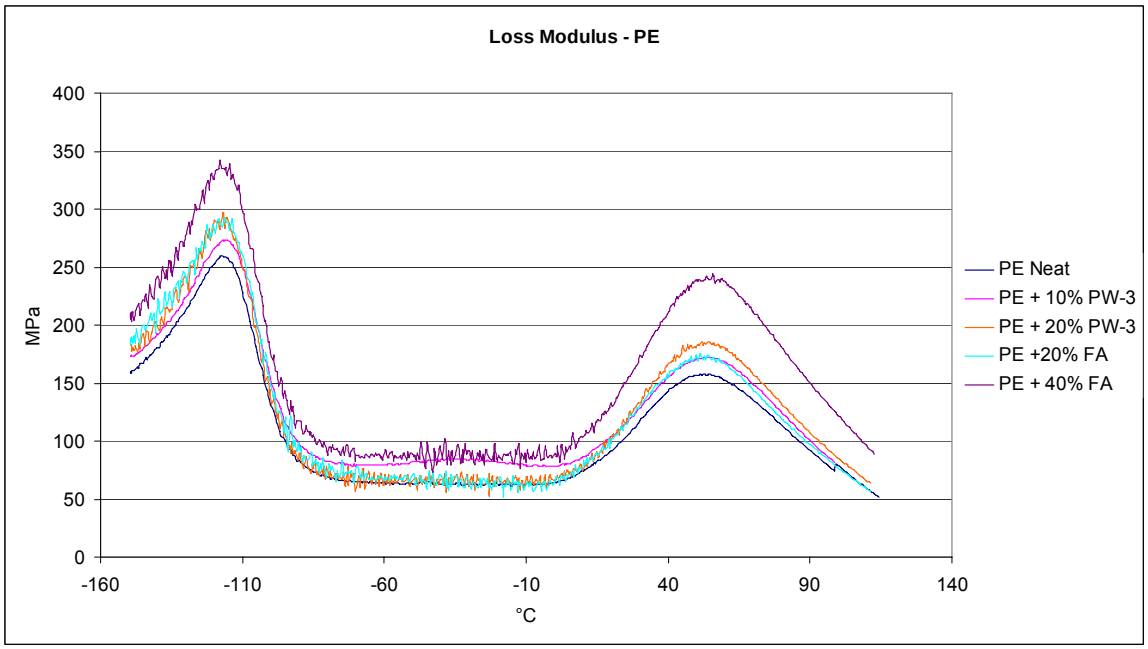


Figure 8. Loss Modulus for HDPE and Filled Composites.

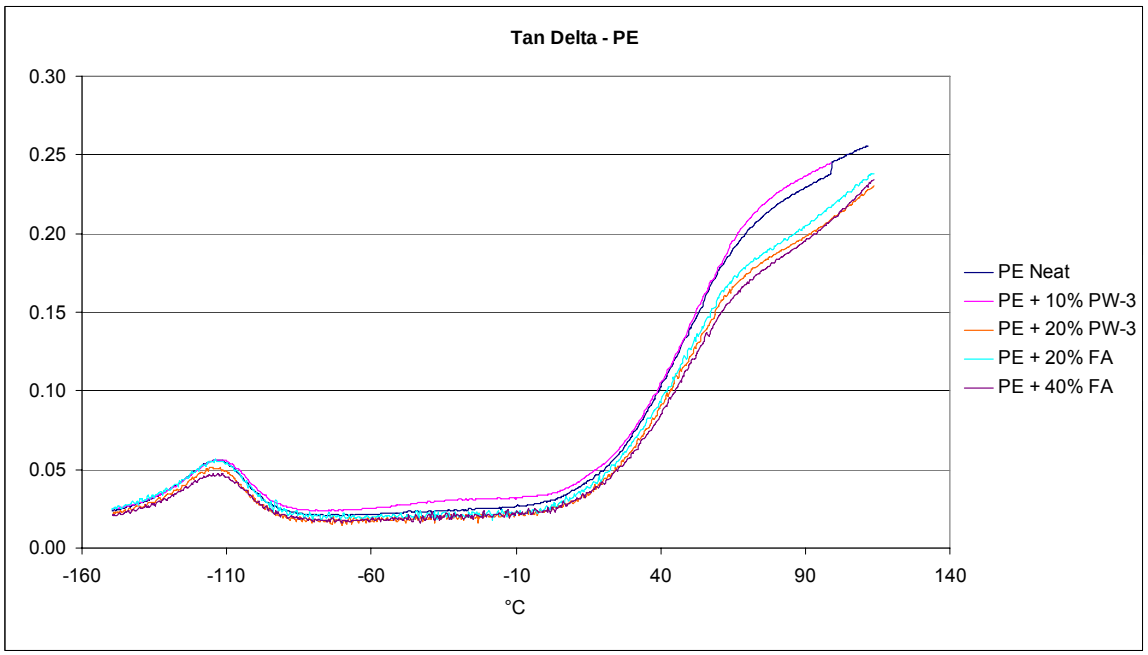


Figure 9. Tan Delta for HDPE and Filled Composites.

Although there are some alterations in the properties of the HDPE with the addition of both fillers ($CaCO_3$ and fly ash), the alterations are small. More importantly, the transition temperatures are not altered.

Figures 10, 11 and 12 show the results obtained for Santoprene TPE.

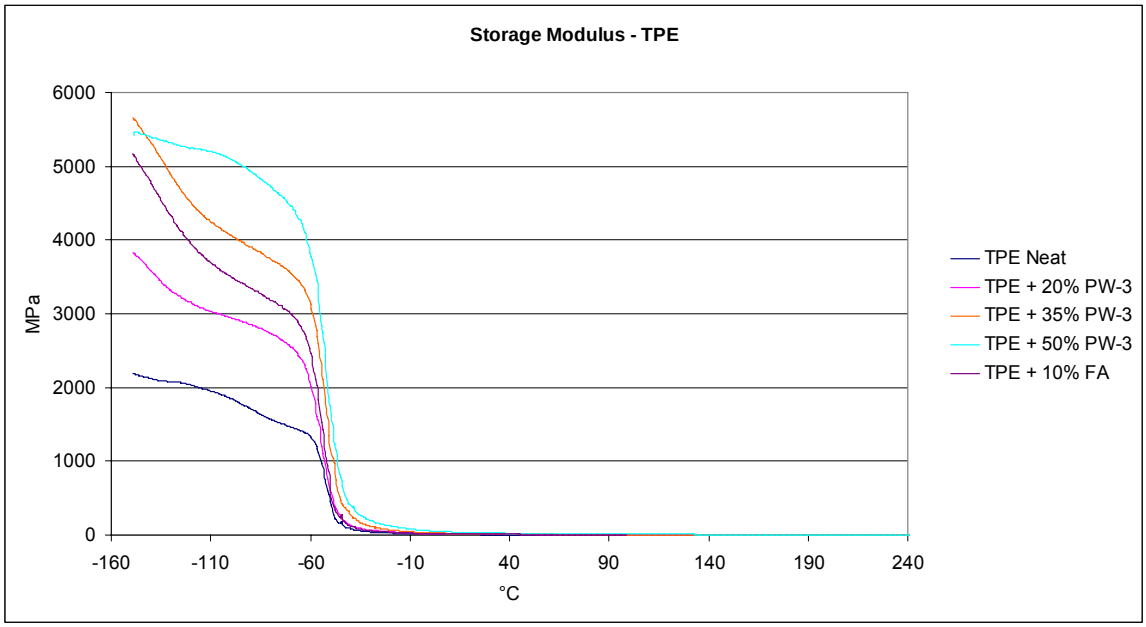


Figure 10. Storage Modulus for TPE and Filled Composites.

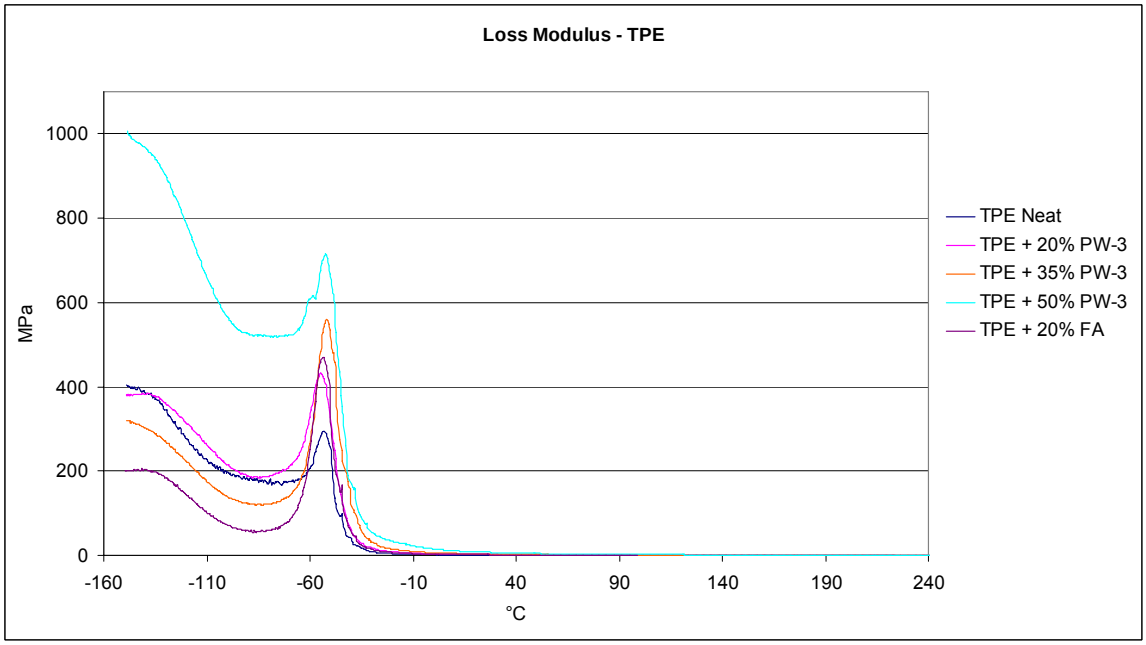


Figure 11. Loss Modulus for TP and Filled Composites.

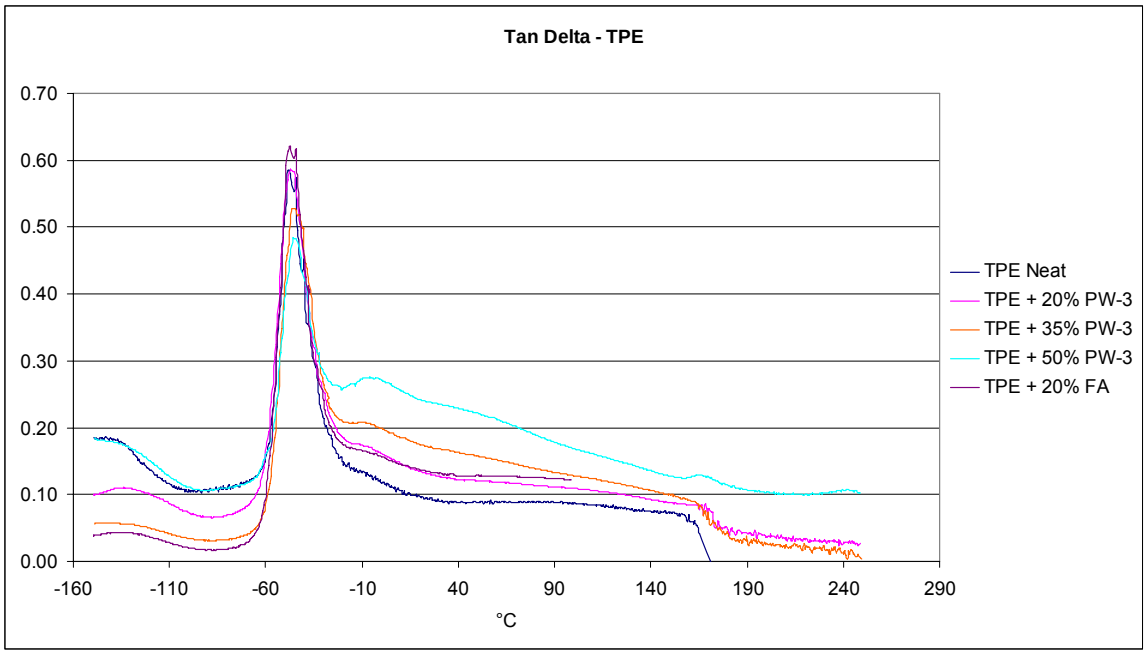


Figure 12. Tan Delta for TPE and Filled Composites.

Again, there are some alterations in the properties of the composites compared to the pure polymer but the transition temperatures are not altered.

Summary

As mentioned above, the addition of fillers creates a composite material with different properties than the polymer alone. The suitability of the composite for a particular application must be evaluated in terms of all of the properties altered and which compromises are acceptable.

These preliminary results all indicate the tensile properties of the polymers are altered by the addition of ultra-fine fly ash and commercially available calcium carbonate in the same manner and to similar degrees. A full panel will include similar filler loadings of both Omya PW-3 calcium carbonate and ultra-fine fly ash in HDPE, Santoprene-55 and polyethylene terephthalate (PET). Also, the fillers will be treated with titanate and silane based coupling agents which improve the bonding of the filler to the polymer by lowering the surface energy and facilitating wetting. It is expected that the use of coupling agents will significantly alter the effect of filler on the composites, especially on the tensile properties.

Glossary of Terms and Abbreviations

DMA	Dynamic Mechanical Analysis
E*	Complex Modulus
E”	Viscous or Loss Modulus
E’	Storage Modulus
HDPE	High Density Polyethylene
Omya PW-3	Reference Calcium Carbonate Filler
PET	Polyethylene Terephthalate
T_g	Glass Transition Temperature
TPE	Thermoplastic Elastomer